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MULTI-SCALE SIMULATION OF SOFT MATERIAL FLOW

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ABSTRACT

We describe a multi-scale modeling approach to model the rheology of soft matter, which can then be applied to simulate flow of viscous inorganic material in pipes and containers. Mesoscale methods, such as dissipative particle dynamics (DPD) are a key component of multi-scale modeling, as they bridge the gap between fundamental theory and continuum length scales.

The paper describes a method for parameterizing DPD simulations for cements and inorganic sludges based on calculating a volume dependent cohesive energy interaction and compressive term from MD simulation with a generalized inorganic forcefield. By modifying the fluid properties through the interaction parameters one can simulate change of chemistry, such as pH or the introduction of chemicals to improve flow properties (super-plasticizers). Parameters obtained from mesoscale simulation can then be applied to simulate flow of soft matter inside pipes and containers using traditional CFD techniques. Two potential future applications in the nuclear industry are discussed in the areas of waste retrieval and encapsulation.

INTRODUCTION

Predicting the physical properties of materials is a problem faced by the nuclear industry. Trials involving radioactive materials are expensive and we need to ensure that simulants are representative of waste forms. An area of particular concern, when investigating options for the retrieval and storage of legacy wastes, is the rheological, physical and structural properties of inorganic slurries and soft materials. One area where issues could occur is with the pumping of radioactive slurries, retrieved from legacy waste tanks.

In materials such as slurries and cements, the underlying molecular structure is very complex. Inorganic material is typically suspended in the fluid phase, or coagulated into colloids or gels. The physical and structural properties of these materials are determined at meso length (10^{-6} to 10^{-2}m) and time scales (10^{-8} to 10^{-4}s). However, the reason why these materials behave as they do is determined by chemistry and physics at shorter nano length scales, nano-length (10^{-10} to 10^{-8}m) and time scales (10^{-15} to 10^{-10}s). Rheology is concerned with the flow behavior of all types of matter. It determines how materials can be poured or reshaped. The rheological behavior of a material is determined by the interaction between the molecules and particles in the material, and thus is controlled by the chemistry. Whilst methods such as molecular dynamics contain the chemistry and physics necessary to investigate the rheological properties of these materials, we are prevented from applying these techniques by the computational cost of bridging the gap between the nano and meso length scales. Novel multi-scale modeling methods have the potential to bridge this gap.

One of the emerging mesoscale modeling methods is Dissipative Particle Dynamics (DPD). DPD became established by Groot and Warren (GW)[1], and has principally been applied to the simulation of problems common to the polymer industry, such as phase separation and the effect of surfactants. Though in fact it is a generalized mesoscale approach that can be used to obtain structural and rheological properties of many types of materials.

The method that we will discuss in this paper follows a more generalized parameterization of dissipative particle

dynamics, that is first described in the paper of Good et al[2]. The method initially follows the derivations of McGrother[3] and GW[1], but deviates from these methods to include a more generalized description of solubility based on the regular solution theory of Hildebrand[4]. This derivation is significant as it moves away from the Flory-Huggins parameterization of dissipative particle dynamics simulation adopted by polymer scientists. The principle advantage of this approach is in the mathematical representation of the like-like bead interaction parameters for a material.

Our parameterization follows a 'bottom-up' approach, where we have calculated the interaction parameters from molecular dynamics simulations, applying a generalized inorganic forcefield[5]. The key advantage of this coarse-grained approach is that it provides a theoretical underpinning of the dissipative particle dynamics method; Material properties computed by this approach can be linked back to differences in the underlying molecular structure, without this being explicitly included in the simulation.

We describe an application of dissipative particle dynamics for the modeling of a suspension of silica (SiO_2) in water. The system is a useful model to test the method of parameterizing dissipative particle dynamics models of inorganic systems, as the properties computed by DPD can be compared directly against experimental data. The simulations we are presenting in this paper represent our first attempts at following the new methodology to simulate a complex inorganic system. This represents a challenging problem for the technique as suspensions of this type show complex rheological behavior. We will show how the method can be practically applied describing the procedure for deriving the interaction terms. We have applied this method to determine both structural and rheological properties of the suspensions generated, and qualitatively have compared the results against experiment. As the work presented here represents the current status of progress with the method, we will also discuss the areas that need further development.

NOMENCLATURE

DPD - Dissipative Particle Dynamics
MD - Molecular Dynamics
$g(r)$ - Radial distribution function of inter bead distances
a - DPD conservative interaction term
γ - DPD dissipative interaction term
χ - Helmholtz free energy derived solubility parameter
K - Bulk modulus
η - Viscosity
(v/v)% - Volume percent
ρ - Number density of DPD beads
κ - Isothermal compressibility

METHODS

DPD simulations of the structure and rheology of inorganic suspensions

In a DPD simulation, a material is represented by a set of particles or "beads". A single DPD particle may represent anything from a few atoms to millions of atoms. For an inorganic suspension, separate DPD particles may represent clumps of oxide material, e.g. $(SiO_2)_n$, and regions of the fluid phase (water). DPD offers a true mesoscopic representation of a system. DPD mass and length units are non-dimensionalised. The bead mass and radius is arbitrarily chosen, but should be chosen as to represent the structure and physical properties of the system you are investigating. Due to the coarse grained nature of the interaction parameters, which are in turn related to bulk properties of the system, as we will describe later, it is possible that there is a minimum real particle size that a DPD bead can represent. Similarly, in choosing a larger bead size, some structural detail would be lost and the physical properties of the system would be similarly altered.

The particles in DPD interact through a sum of three different forces: a conservative force, a dissipative force and a random force. Inclusion of the latter two forces distinguishes DPD from Molecular Dynamics. They essentially build the correct hydrodynamic behavior into the model.

The conservative force is typically a (pairwise additive) soft repulsive interaction parameterized through a single repulsion parameter, a, and a parameter which determines the range of the interaction (the cut-off distance), r_c. Within an additive constant, the DPD potential describing the interaction between a pair of beads can be written as

$$\boldsymbol{\Phi} = \begin{cases} \frac{a}{2}\left(1-\frac{r}{r_c}\right)^2 & r \le r_c \\ 0 & r > r_c \end{cases} \qquad (1)$$

where r is the scalar separation between a pair of DPD beads. The chemistry of the system is captured within this single repulsive parameter.

The random force adds thermal noise to the model. The magnitude of the random force is determined by the σ parameter. The dissipative force includes the fluid interactions, and represents the viscous drag. The magnitude of the dissipative force is determined by the γ term. The dissipative and random terms are related through fluctuation-dissipation theorem by

$$\sigma^2 = 2k_B T\rho\gamma \qquad (2)$$

The hydrodynamic behavior of the fluid, which gives rise to physical properties of the diffusivity and viscosity, is captured within the γ parameter. Together, the dissipative and random forces act as a thermostat, to keep the simulation temperature fixed around an average value.

For single component systems only one repulsive parameter is required. Multi-component mixtures require specification of a matrix of repulsion parameters describing the

interaction between each pair of species. For example, in a system of two components, *i* and *j*, this gives rise to a simple matrix of interaction parameters representing *ii*, *ij* and *jj* interactions. By modifying the ratio between the interaction parameters, DPD can be used to represent gel phases, walls and separated phases such as colloidal suspensions. The physical and chemical changes represented by changes in the interaction parameters is fairly subtle. Large differences in the *ii* and *jj* terms can result in phase separation.

In the standard implementation of DPD, the soft repulsive parameter is obtained by first calculating an equation of state of the DPD fluid for a range of values of this parameter. A plot of excess pressure divided by $a\rho^2$ versus ρ is then constructed. The asymptotic limit of this plot then establishes a value for α, which, although it is treated as an empirical parameter, is actually related to the integral of the product of the soft potential and the radial distribution function. The equation of state of the DPD system can then be stated as

$$p = \rho k_B T + \alpha a \rho^2 r_c^4 \qquad (3)$$

Where ρ is the number density of particles. The next step is to equate the compressibility of the DPD fluid to that of the material of interest, thus ensuring that the former has the same fluctuations as the latter. In practice non-dimensional inverse isothermal compressibilities are equated. The non-dimensional inverse compressibility, κ^{-1}, is defined by

$$\kappa^{-1} = \frac{1}{\rho k_B T \kappa_T} = \frac{1}{k_B T}\left(\frac{\partial p}{\partial \rho}\right)_T \qquad (4)$$

where κ_T is the usual isothermal compressibility. By differentiating equation (3) with respect to the number density and dividing through by k_BT we obtain the expression for the inverse dimensionless compressibility of the DPD fluid. In the original work of GW[1], the DPD fluid was parameterized with respect to water, which has a κ^{-1} value ≈16. Thus we obtain the operational equation for a

$$a = \frac{75 k_B T}{\rho r_c^4} \qquad (5)$$

Within a DPD simulation, it is common to set r_c to 1. Hence we can define the dimensionless a parameter $\overline{a}$ by

$$\overline{a} = \frac{75}{\overline{\rho}} \qquad (6)$$

Where $\overline{\rho}$ is the dimensionless density, defined by $\overline{\rho} = \rho r_c^3$. It is noted that $\overline{a}$ is constant for a given compressibility but scales as the reduced number density. With the choice of $\overline{\rho}$=3, a dimensionless value of $\overline{a} \approx 25$ was obtained. This scaling of DPD particle size allows multi-bead interactions to be incorporated into DPD, as several beads will be present within r_c=1. The vast majority of DPD papers published since the original GW paper have used the same value for the repulsive parameter, regardless of the system being studied. The compressibility of all bead types is fixed to a single value to conform to the lattice based Flory-Huggins model of polymer fluids. The interaction parameters for unlike species are obtained by appealing to Flory-Huggins theory, and entails calculating solubility parameters.

Recently, Good *et al* have extended DPD to simulate inorganic systems by modifying the procedure through which the repulsive interactions are obtained[2]. Their method, while similar to the original GW approach, contains several significant differences. The first major difference is that the repulsive interactions between like species are allowed to differ; Thus the value for *ii* interactions maybe different from that of *jj,* say. Each of these interactions has its own repulsive parameter that must be determined by the procedure outlined above and involves calculating compressibilities (or bulk modulii) for every species from atomistic simulations or using experimental values where available. The next crucial step in the method of Good and co-workers was to determine what they termed 'compressive' contributions to the interactions for unlike species. The compressive contributions to the repulsive interactions of unlike species were determined from the geometric mean of the parameters for the *same* species. Thus $a^c{}_{ij} = \sqrt{a^c{}_{ii} a^c{}_{jj}}$, where the *i* and *j* refer to species *i* and *j*. This choice for the combining rule was justified by appealing to Hildebrand's regular solution theory[4].

The final step in the parameterisation method developed by Good *et al* involves modifying the $a^c{}_{ij}$ parameters to account for differences in the solubility of one species in another which essentially takes attractive interactions into account implicitly (by lowering the mutual repulsion felt between a pair of unlike molecules). The free energy of mixing of a pair of equal volume liquids can be shown to depend linearly on the 'solubility' interaction parameter, $a^s{}_{ij}$. However, since the free energy of mixing is also related to the solubility, a linear relation exists between the solubility and the solubility part of the repulsive parameter for unlike species:

$$\chi_{ij} = 2\rho\alpha a^s{}_{ij} \qquad (7)$$

Solubilities relate to the cohesive energy density, a bulk property of the solid or fluid that can be calculated from atomistic simulations (we describe the procedure later in this article). Once these are determined, the $a^s{}_{ij}$ terms are readily calculated using the above equation (once the α parameter has been determined empirically). We note that a positive value of $a^s{}_{ij}$ will result in de-mixing. In summary then, the total interaction parameter for unlike species is obtained via:

$$a^{tot}{}_{ij} = \sqrt{a^c{}_{ii} a^c{}_{jj}} + a^s{}_{ij} \qquad (8)$$

So far we have concentrated on the a parameter which defines the conservative interaction but have ignored the γ parameter which defines the hydrodynamics of the fluid. If we consider that the *a* parameter introduces the chemistry into a DPD model then the γ parameter introduces the physics. The relative viscosity of a fluid is determined by the chemistry of the system, this is incorporated within the *a* parameter. It is thus possible to extract relative information on shear viscosities by choosing a fixed value of γ. As equation 2 includes the number

density, we find that as for $\bar{a}$, $\bar{\gamma}$ is proportional to $\bar{\rho}$. The value typically chosen for $\bar{\gamma}$ in a DPD simulation is 4.5. As will be shown later, for a value of $\bar{\rho}$=3 this results in a calculated dynamic viscosity of water, from a simulation at nominally 25°C, approximately a factor of 10 lower than that quoted for the experimental value.

A lower value of $\bar{\gamma}$ is likely to lead to a more rapid approach to equilibrium in the DPD system, leading to shorter simulation times, particularly for suspensions at low shear rates. Relative rheological data can be extracted from relative viscosities and fitted to a mathematical relationship, such as that defined by the Krieger-Dougherty relationship, as will be discussed later.

We have now defined the complete set of a interaction parameters for a 2 by 2 matrix of species, and this is listed fully in table 1 for reference. Through the equations we have given in this text, the parameters in table 1 can be directly computed from two bulk properties of the fluid or solid, namely the bulk modulus of the material and the cohesive energy of the material. In the following section we will go on to describe how we can obtain these parameters from a molecular dynamics simulation, completing the multi-scale description of our complex fluid.

Table 1

Matrix of conservative interaction parameters for a DPD simulation for a system of two components (i & j) following the method of Good[2].

Bead type	***i***	***j***
i	a^{c}_{ii}	$\sqrt{\left(a^{c}_{ii}a^{c}_{jj}\right)} + a^{s}_{ij}$
j	$\sqrt{\left(a^{c}_{ii}a^{c}_{jj}\right)} + a^{s}_{ij}$	a^{c}_{ii}

Simulation details

In this study we have conducted a series of DPD simulations of the silica /water system at various volume fractions of silica. Two different types of DPD particles were introduced to represent water and silica respectively. The different types of DPD beads have equal volumes. The particle size that a DPD particle represents can in principle be arbitrary. Making the beads larger introduces a greater degree of course graining: each bead representing more fundamental building blocks, which may for example, be water molecules.

Since all particles have the same interaction range, r_c, this serves as a characteristic length scale in DPD. It is common practice use the value of k_BT to establish a unit of energy and for the particle mass to be the characteristic unit of mass. DPD simulations are conducted in dimensionless units. The relationship between some of these dimensionless units (denoted by a bar overstrike) and their real unit counterparts are given below

$$\bar{r} = r/r_c,\ \bar{t} = t\sqrt{\frac{k_BT}{mr_c^2}},,\ \bar{\eta} = \frac{\eta\, r_c^2}{\sqrt{mk_BT}} \quad (9)$$

Where r is the scalar distance between a pair of particles, and η is the dynamic viscosity. In keeping with other DPD simulations we have simulated conditions in which the DPD temperature, $\bar{T}$ = 1. To study materials at different temperatures one must modify the interaction term matrix, according to the effect of temperature on the solubility and compressibility. All of the simulations carried out is this study correspond to a real temperature of 298 K.

The DPD code supplied by Accelrys Inc.[6] was used to carry out the simulations described in this paper. The inclusion of relatively large interaction parameters determined by this method to describe the inorganic and inorganic/ aqueous interactions requires that the time step be reduced, with respect to typical values used in a polymer simulation, to allow equilibrium to be attained for a limited number of particles. DPD interaction parameters were calculated from molecular dynamics using the procedure described in the following section.

Simulations were run on system sizes of 1537 beads, in a periodic system of 8 DPD units cubed with a DPD density of 3.0. The simulations were run for 120,000 time steps, with a time interval of 0.025. We will discuss mapping on to real units of length and time later in the paper. The time step was carefully chosen to avoid issues with thermostat control, due to the large conservative forces. They were established by ensuring the standard deviation in the thermostat was not significantly greater than 0.1, even at high shear rates.

In order to obtain the viscosity of the silica suspensions we conducted a series of DPD simulations in which the particles were subjected to planar Couette flow (this is accomplished within the Accelrys code by applying Lees-Edwards boundary conditions). The shear stress, σ_{xz} was calculated from the virial theorem every 300 DPD time steps, and then averaged. The viscosity was then calculated from the linear constitutive relative:

$$\eta = \frac{\sigma_{xz}}{\lambda} \quad (10)$$

where η represents the dynamic viscosity and λ is the shear rate. It is important to note that the shear stress given by the Accelrys DPD code gives a value from the pressure tensor that has been normalized by the density. To obtain the true value of the shear viscosity we have to multiply this value by the DPD bead density, set at 3.0 in all of our simulations. The dissipative term, $\bar{\gamma}$, is set to 4.5 in our simulations.

We varied the shear rate between 0.05 and 2.0 DPD units, equivalent to real shear rates between 50 and 1000s^{-1}, according to the scaling argument that will be discussed later. A range of silica suspensions was studied ranging 0 to 40 %, by volume of silica. The structural properties of the suspensions generated in the shear simulations were analyzed by generating graphical images in MS modeling 3.2. Radial distribution functions, *g(r)*,

were generated from the exported MS modeling structures using an in-house code. The method employed followed that given in Allen and Tildesley, for the generation of *g(r)* from a normalized histogram of the inter-bead distances[7].

We have normalized our interaction parameters in terms of the volume and mass of individual water or silica molecules. In doing so, we loose the physical units of length, mass and time. In order to extract physical properties from these simulations we will need a method to re-dimensionalize the results from the DPD simulations from reduced units to real units so our simulation results can represent a real physical system. Note that you are not limited to re-dimensionalizing according to the original coarse graining bead size. Our choice of bead size, in terms of mass and volume determines the physical properties we are attempting to map the dimensionless DPD results to. One should choose a redimensionalizing bead size that is comparable to the real physical system. We will comparing the results of our DPD simulations against a silica water suspensions, which studied experimentally by Zaman *et. al.*[10]. In this paper, rheological properties are given for aqueous suspensions of silica particles of 0.3μm radius. This is used to set the particle size that a DPD bead will represent in our simulations.

We need to understand how physical units scale in terms of the real particle size each bead represents. This problem has been investigated in several papers, notably that of Groot and Rabone[9]. We differ slightly in their approach by defining N_r as being the factor by which the normalizing radius r_c (for an SiO_2 molecule) is scaled to represent our real bead size. Thus for N_r=500, we have a real bead size 500 times the radius of SiO_2. Note that N_r=1 is not the atomistic limit, as the DPD fluid always remains a molecular substitute material, due to the coarse graining.

The two units that characterize the rheology of our system are time (the inverse of which defines the shear rate) and viscosity. By investigating the how the diffusivity and viscosity of our nominal water fluid, defined by $\overline{a}$=25 and $\overline{\gamma}$=4.5 scale according to increasing N_r, we have arrived at a scaling relationship of $\sqrt{N_r}$ for both physical quantities. This scaling is related to the square-root of the mass, equation 9. Hence, we can set the scaling of the unit of time to be $\sqrt{N_r}$ and that of the shear rate to be $1/\sqrt{N_r}$. For a water bead radius of 0.3μm, this sets the DPD unit time to be equivalent to 1ms. For a simulation of 120,000 steps at a DPD time step of 0.025, corresponding to a real time of 0.8ms. The length of the simulation is 3s in real time.

The volume of a water molecule is 30Å^3 and the volume of a silica molecule 40Å^3. The radius of the molecule r_m is approximately the cubed-root of the volume. This scales as $N_r r_m$. The bead mass is determined from the volume of a sphere of 0.3μm radius and the density of each component. the density of each component, 0.987g cm^{-3} for water and 2.54g cm^{-3} for silica, assuming spherical particles. For simulations where we have a mixture of silica and water, number fraction weighted average quantities for the molecules mass, radius and volume, by calculated. The volume fraction is simply the number fraction in the simulation as we have assumed equal volumes of each bead.

DPD parameterisation from molecular dynamics

A method has been developed for calculating the interaction parameters required for a dissipative particle dynamics simulation from the bulk modulus of the material and the cohesive energy. These parameters can be computed for a aqueous suspension of silica directly from molecular dynamics simulation. A number of academic and commercial codes have been implemented for conducting the simulations. We have used the Discover code from Accelrys Inc.[6] for all of the molecular dynamics simulations described in this paper, employing a generalized forcefield, CLAYFF, developed by Cygan[5], to describe the silica/ water system. We have tested the forcefield against a range of metal oxides and metal hydroxides. It was found that it was able to reproduce the lattice parameters of quartz (SiO_2) to within 2% of experiment.

The compressibility of each component was calculated by conducting a series of NVT molecular dynamics simulations at a range of densities, and calculating the pressure in each case. An empirical equation was then fitted to the pressure versus density data from which the derivative at the density of interest was obtained. This value can then be related to the isothermal compressibility via eq. 4. Once the compressibilities were determined, the compressive contributions to the repulsive parameter for silica-silica, silica-water and water-water interactions were then obtained followed the procedure outlined earlier and summarized in Table 1.

The solubilities of water and silica were also obtained from atomistic simulations using a procedure outlined by Maiti and McGrother[3] for the simulation of polymer mixtures. Briefly, the procedure is as follows. Amorphous molecular structures were generated for pure silica and pure water phases using the Amorphous Cell code[6] in Materials Studio. These simulations comprised 100 water or SiO_2 units. These initial structures were then annealed using molecular dynamics in the NVT ensemble until thermodynamic equilibrium was established. The cohesive energy of each phase was then obtained from

$$\Delta E = \Sigma_n E^{gas} - \left(E^{solid}\right)_n \qquad (11)$$

where E^{gas} and E^{solid} are respectively the total energies of the gas and condensed phases. The gas phase energy represents the total energy in the absence of inter-molecular interactions. This can be computed from a molecular dynamics simulation of a single molecule in a large periodic box.

In generating these structures, we have chosen experimental values of density of 2.54g cm^{-3} for silicon oxide and 0.987g cm^{-3} for water. These densities determine the volume terms used to non-dimensionalize the cohesive energy density and compressibility terms. The choice of 100 molecules in the simulation box was obtained after a systematic study involving system sizes ranging from 100-400 molecules. It was

observed that the standard deviation in the cohesive energy density was less that 1 kJ cm^{-3} and hence a system size of 100 represents a reasonable trade-off between accuracy and computational efficiency.

The next step in the calculation involves determining the energy of the mixed phases. In these simulations, amorphous cells are built containing a single molecule of one species and 100 molecules of the other species (1%). The mixing energy of any composition is then obtained by linear interpolation of the two end points (1% and 100%). So the energy of mixing of the one phase in another ΔE_{AB}^{mix}, is given by

$$\Delta E_{AB}^{mix} = \left(n_A \Delta E_A^{main} + n_B \Delta E_B^{main} \right) - \Delta E_{AB}^{calc} \qquad (12)$$

ΔE_A^{main} is the energy of the pure phase weighted by the number fraction in the mixed phase n_A and ΔE_{AB}^{calc} is the energy obtained from the simulation of the mixed phase. The non-dimensionalised cohesive energy gives us the χ_{ij}^{cs} parameter for the DPD solubility interaction parameter:

$$\chi_{AB}^{cs} = \frac{V}{k_B T} \Delta E_{AB} \qquad (13)$$

where V is the volume of one molecule of one of the components in the suspension. In applying this equation, we non-dimensionalize the cohesive energy density to a single bead volume. In coarse graining our system, we have lost some chemical detail in particular due to the directional nature of some of the non-bonded interactions (Van der Waals and electrostatic forces). This is especially true for water in our system. Also, we have excluded any description of covalent forces due to bonds formed between particles, through this is certainly possible in DPD and is included in the Accelrys code.

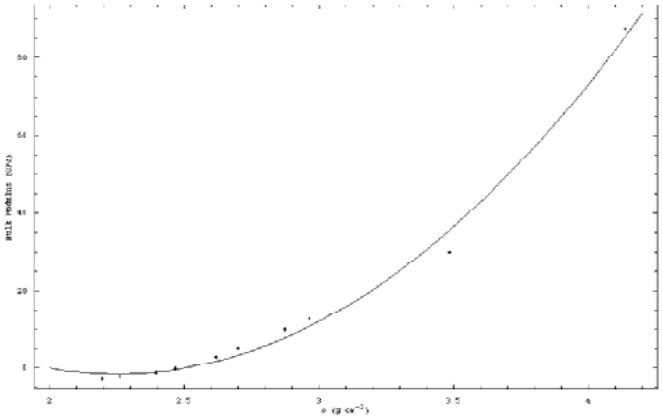
RESULTS

We had some success applying molecular dynamics to calculate the bulk properties of the materials for our DPD simulation. The calculated bulk modulus of water was 2.19GPa, at a density of 0.987 g cm^{-3}. This is identical to the value obtained from experiment and shows that the forcefield and simulation employed was adequate. It was found that the molecular dynamics simulation did reproduce the bulk modulus of SiO_2 at this density, a value of 36.94GPa was found at a density of 2.2g cm^{-3}, shown by the plot in figure 1. The experimental value of the bulk modulus of amorphous SiO_2 is 37.02GPa, at a density of 2.54g cm^{-3}. The error is within the range expected from our determination of the lattice constant of quartz using this forcefield. The cohesive energy densities of water and amorphous silicon oxide were the first energetic parameters computed by molecular dynamics. The cohesive energy density of water was calculated as 2.29 kJ cm^{-3}, and that for silicon oxide was 21.21 kJ cm^{-3}. The value computed for water shows reasonable agreement with the experimentally quoted value of 2.2 kJ cm^{-3}.

When we applied these parameters to our DPD simulations, some promising results were obtained. The value of $\overline{a}$ for water for $\overline{\rho}$=3, from a bulk modulus of water of 2.19GPa at 25^{o}c, following our method was determined to be 25.106. This value was used to investigate the viscosity of water as a function of shear rate. The DPD simulation involved 1537 particles, for 120,000 DPD steps at a time step of 0.025. This simulation was repeated for shear rates of 0.05 to 0.9 DPD units. The shear viscosity was calculated in reduced units from the average of the σ_{xz} stress tensor according to equation 10. These results were re-dimensionalized by choosing a real bead size of N_r=1000, corresponding to a fluid particle diameter of 0.6μm. We apply the scaling laws for the shear viscosity, shear rate and time. The value of N_r was varied to confirm that The viscosity remained constant. The results are shown in figure 2. The DPD simulation predicts that water is a Newtonian fluid over the range 50 to 1000s^{-1}. The calculated viscosity is 1×10^{-5}Pa s, over a factor of 10 lower than the experimentally quoted value of 8.6×10^{-5}Pa s. To obtain a quantities match, one would have to match the value of the dissipative term $\overline{\gamma}$ and $\overline{\rho}$ to the experimental viscosity of water.

Figure 1

Plots of the bulk modulus of amorphous silica calculated from molecular mechanics, CLAYFF forcefield[5] and Discover code[6].

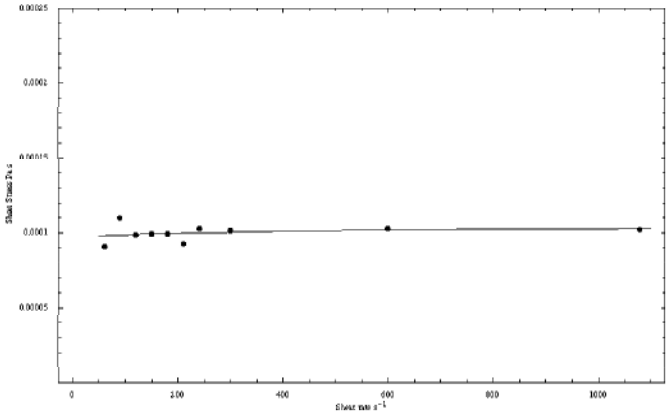


The results from the simulation of silica suspensions were initially analyzed to obtain structural information. A picture generated from MS Modeling 3.2 of the 20(v/v)% silica simulation, after undergoing shear at 0.01 DPD units, is shown in figure 3. It can be seen that there is a tendency for the silica beads to group together, and a solid structure has formed at the centre of the 3-dimensional box. Two distinct phases are visible: one consisting primarily of silica and the other of water. Note that some mixing between these phases has occurred. The silica phase appears to show an irregular order. The boundary conditions have apparently had an impact on the structure of the silica phase, resulting in the formation of a silica 'band'. At lower volume fractions (not shown) a more distinct silica 'particle' was formed at the centre of the box. Another useful method of analyzing the structures obtained is to generate contour plots of the bead density in MS Modeling. A plot of the density of the 20(v/v)% suspension, after shearing at low (0.01

DPD units) and high (0.25 DPD units) shear rates is shown in figure 4. The two phases have clearly separated into distinct bands, reflecting what was observed from figure 3.

Figure 2

Plot of the dynamic viscosity of water. The trend clearly exhibits Newtonian behavior though noise is present at low shear rates. The mean dynamic viscosity is 1×10^{-5}Pa s, significantly lower than the value normally quoted experimentally for water at this temperature of 8.6×10^{-5}Pa s. This is the result of choosing a low value for $\dot{\gamma}$ in the simulations.



Radial distribution plots gave a clearer picture of the underlying structures formed. The plots obtained for the 20(v/v)% silica-water suspension is shown in figure 5. This result is following shearing at 0.1 DPD units, and the *g(r)* value was averaged over a number of frames generated in the simulation. The plots showed that there was some underlying order in the silica phase that has formed, whilst the underling structure is clearly amorphous. The peak in the *g(r)* value for silica is an indication of some close range order, as 1 is the diameter of a DPD bead. The smaller peaks at 1.4, 1.6 and 2.6 units indicate that there is also some secondary order, indicating that clumps of silica particles have formed in the simulation. The water phase is clearly amorphous, and a significant proportion of the bead-bead distances are less than 1, showing that there has been significant compression of this phase. No attempt was made to determine the effect of simulation size, or time, to determine the impact of these factors on the structures formed.

Plotting *g(r)* for the silica-water interaction, figure 6, shows there is a significant interaction between the water and silica beads, signified by the peak at 1 DPD units. Shearing the system at a higher shear rate increases the degree of mixing between the phases, as represented by the slight increase in the silica-water peaks at 1 and 1.75 units. Viewing the 3D structure in MS Modeling, it was confirmed that a proportion of the water has dispersed within the silica phase, and so this does not represent a solid silica phase.

The results obtained from the first series of simulations on the rheology of silica suspensions are shown in figure 7. It can be seen that at low silica volume fractions, the viscosity is independent of shear rate, the trend lines shown on figure 7 are linear functions. This means that the fluid is behaving as Newtonian at these shear rates. At high silica volume fractions, there is a change in rheological behavior at low shear rates. In the plots shown in figure 7 we have kept the system in reduced DPD units to illustrate general behavior.

Figure 3

Image generated in MS Modeling 3.0 of a 20(v/v)% silica suspension in water. The SiO_2 beads are shown at full size (red), the water beads are shown at 0.4 radius (image shown 45° to axis). Shear is applied in the horizontal direction.

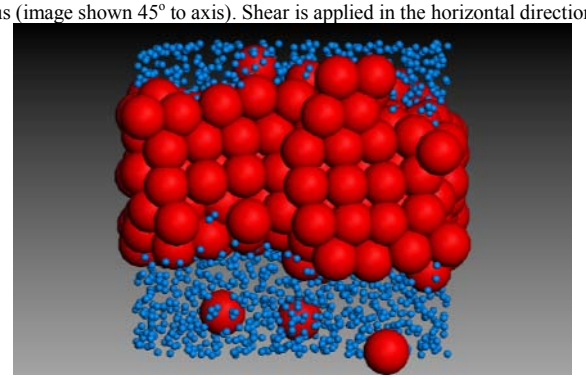
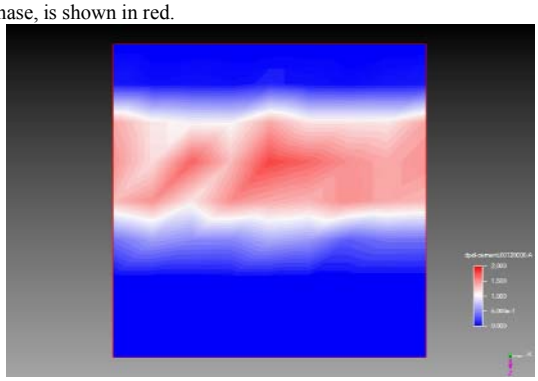


Figure 4

Contour plot generated from MS Modeling showing the density of silica in a 20(v/v)% suspension. The high density region, which shows the 'banding' of the silica phase, is shown in red.



Shear thinning behavior commonly arises in strongly interacting colloidal suspensions, where the viscosity is described by the Ostwald-DeWaele power law[8]. The trend lines shown on figure 6 are the reduced viscosity fitted to a power-law relationship, mx^{n-1}, for 10, 20 and 40(v/v)% suspensions of silica in water. The power law index, *n*, is indicative of the materials rheological behavior. Where *n* is negative. This behavior is described as shear thinning, and is non-Newtonian[9]. As the value for n for 40(v/v)% is 0.5, this shows pseudo-plastic behavior. The power-law indices for the 20 and 10(v/v)% suspensions show power-law indices of ~1, and are indicative of a Newtonian fluid. The slight downward trend observed at 20(v/v)% at low shear rates is probably an indication of statistical noise at low shear rates. The trend shown in figure 6 shows acceptable agreement with published experimental studies of the shear viscosity of silica nano-particulate suspensions, given in the paper of Zaman et. al.[11]. This

experimental data appears to show a transition between Newtonian to non-Newtonian rheological behavior in silica suspensions between 30 and 40(v/v)%. The plot of the 30(v/v)% rheology is not shown to make the plot clearer.

Figure 5

Radial distribution function, g(r) for water-water and silica-silica distances computed for a 20(v/v) % silica suspension.

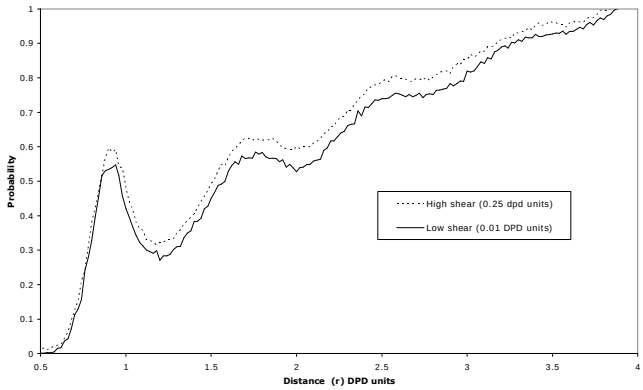
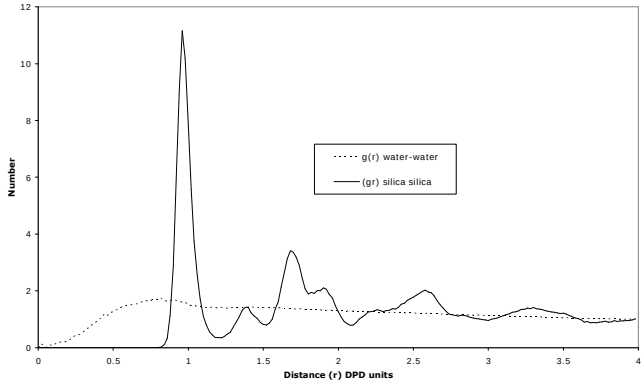


Figure 6

g(r) for silica-water interaction in a 20(v/v)% suspension, corresponding to the density plot shown in figure 4. The first peak corresponds to a water-silica separation of 1 (DPD units) showing that there is some mixing between the bead types.



In mapping on to real units of viscosity and shear rates we have defined a bead size comparable to the silica particles used in the study of Zaman *et. al.*[11], for a diameter of 0.6μm, hence N_r=1000. The Krieger-Dougherty relationship for reduced viscosity of spherical colloidal suspensions is

$$\eta_r = (1-\frac{\phi}{\phi_{eff}})^{-n\phi_{eff}} \quad (14)$$

where ϕ is the volume fraction of solids, ϕ_{eff} is the packing fraction of the spherical particles and η_r, the reduced viscosity is defined as the viscosity of the solution divided by the viscosity of the solvent (water). Zaman gives the parameters of n=3.1 and ϕ_{eff} =0.615 for the higher limiting (1000 s^{-1}) relative shear viscosity of 0.3μm-radius silica particles in an electrolyte solutions at pH9.5.

We apply the scaling laws to obtain viscosity vs shear rate for our silica-water system. We choose a value of the viscosity at the higher limiting shear rate in the simulation, at the last point in the simulations (nominally ~1000s^{-1}, comparable to experiment, however as these are preliminary results not all data was available at this shear rate). The experimental and DPD calculated Krieger-Dougherty trends have been plotted in figure 8. It can be seen that whilst the model data and experimental data show similar trends, the model over-predicts the viscosity at high silica volume fractions. The model data was fitted to the experimental packing fraction quoted by Zaman. The model data gave a value of η_r of 3.8, which is higher than the experimentally quoted value.

Figure 7

Plot of reduced viscosity for 10 (small dashes), 20 (large dashes) and 40(v/v)% (solid line) silica suspensions calculated from the DPD model. There is a transition between Newtonian and non-Newtonian behavior between 20 and 40(v/v)%.

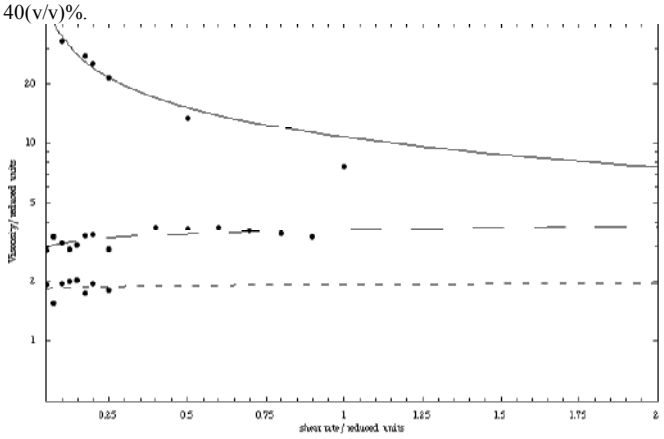
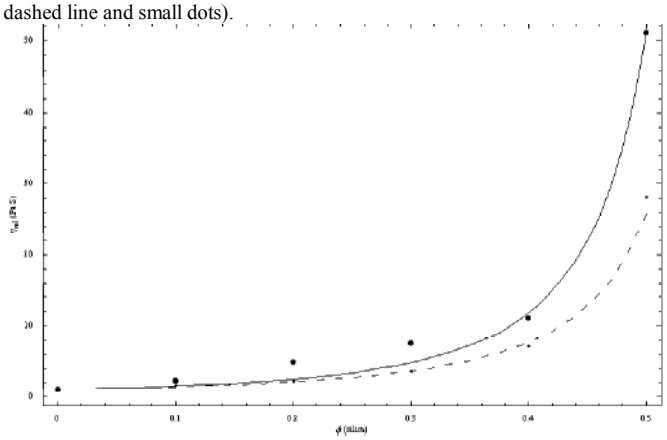


Figure 8

Plot of Krieger-Doherty relationships from DPD model of silica-water (shown as solid line and large dots) and the experimental data of Zaman[11] (shown by dashed line and small dots).



DISCUSSION

The calculation of DPD interaction parameters from molecular mechanics for silica and water, following the method of Good[2] has been successful. We have shown that DPD is not simply a technique for simulating the properties of polymers and their suspensions, and can be applied to solid particles, silica in our studies. Several theoretical approximations assumed in this work require further testing. We have followed the linear approximation originally proposed by Groot Warren[1] for the dependency of the $\overline{a}$ term on χ, given in equation 3. However, it has been suggested elsewhere that a quadratic approximation better represents this relationship at higher values of $\overline{a}$. A factor worth investigating is the use of a linear soft-potential to calculate the force between overlapping beads, equation 1. Other studies have investigated the use of quadratic and Lennard-Jones potentials for particle interactions. Without mapping the dissipative $\overline{\gamma}$ parameter to the fluid, this method is limited to predicting qualitative rheological behavior.

DPD has shown its potential to be a powerful technique for resolving structural information. Identifying structural information from DPD simulations requires the application of various techniques, including 3D structural plotting, density plots and calculated radial distribution functions. Our results have shown that for the silica-water suspension, under shear and at volume fractions greater than 20%, some separation of the phases occurs. By calculating radial distribution functions we have highlighted the order present in the silica phase. The actual structures formed in our simulations may be the result of finite size effects, and this has not been fully investigated.

As we have non-dimensionalised our key interaction parameters in the DPD simulation we have also shown it is possible to "zoom in and out" by changing picking a new particle size to map on to different length and time scales. This lowers the resolution of the available structural information and increases the time step, increasing the period between observable events. We have derived a scaling law which shows how the physical properties (time, viscosity, diffusivity) obtained from a DPD simulation scale with increasing 'real' particle size. Using this method, we have mapped our DPD simulation of aqueous silica suspensions to a particle size of ~0.6μm, and effectively studied rheological properties over time periods of about 3s.

Calculated viscosities that show qualitative agreement with experiment. Generally, the results of the DPD simulations fit the Ostwald-DeWaele power law for rheological behavior. Statistical noise in the DPD simulations does have an affect on the quality of the fit, especially at low shear rates. This does affect the quality of the power law trend fit, and gave little confidence in the ability to extrapolate the results to obtain the viscosity at $1000s^{-1}$. Improving the quality of these results will require longer time scales (more statistical samples) or a shorter DPD time step, The shorter time steps required for simulating DPD species with large interaction terms has not proved to be a problem with respect to computational efficiency. As these represent preliminary results insufficient data was available at high shear rates for all of the simulations, as can be seen in figure 8. As a result of these issues, the Krieger-Dougherty trend was obtained from the DPD simulations by choosing the last available data point. As this in affect represents the reduced viscosity calculated at various shear rates, this does not necessarily represent the limiting high shear rate viscosity. This would account for the overestimation of the trend with respect to experiment at high silica volume fractions, for example.

Despite these issues, the results obtained are highly encouraging in that we have shown that within our definition of the conservative DPD interaction, we have accounted for a transition between Newtonian and non-Newtonian behavior. Comparable rheological behavior has been shown with experiment in that a change from Newtonian to non-Newtonian behavior occurs between 20 and 40(v/v)% silica. The fit to the model data shows a Krieger-Dougherty trend that is broadly comparable to experiment.

CONCLUSIONS

These preliminary studies have given an insight into the potential application of dissipative particle dynamics to study the structural and rheological properties of inorganic suspensions. The results presented in this paper give a strong indication that the method proposed by Good *et. al.*[2] has successfully captured enough of the chemistry and physics of the interactions between the inorganic material and water to describe complex structural and rheological behavior of these suspensions. We have correctly non-dimensionalised the key parameters identified in the paper of Good et al[2], the bulk modulus and cohesive energy density. This has allowed us to use DPD to explore different length and time scales, comparable to experiment.

These results give us confidence in the new method, and whilst some fundamental issues remain to the defining of the underlying physics of some of the interaction terms, we are now confident that dissipative particle dynamics is ready to move from polymer simulations, where it has been traditionally based, to the field of inorganic materials modeling. The ability of the coarse graining technique to capture the chemistry within a single parameter, in turn related to the cohesive energy and the compressibility of the species involved will prove to be extremely useful in simulating complex mixtures. Provided a suitable method of parameterization can be developed, there is no reason to suggest that DPD cannot be applied to resolve the structure of complex solids. Future applications of this technique range from modeling the flow of grouts, to the pumping of waste sludge's from legacy nuclear plants.

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REFERENCES

[1] R. D. Groot and P. B. Warren, J. Chem. Phys. (1997), 107, 4423-4435
[2] K. Good, K. P. Travis, M. Bankhead *in preparation,* (2006).
[3] A. Maiti and S. McGrother, J. Chem. Phys., (2004), 120 no. 3, 1594-1601.
[4] J. H. Hildebrand and S. E. Wood, J. Chem. Phys., (1933), 1 no. 12, 817-822.
[5] R. T. Cygan, J. J. Liang and A. G. Kalinichev, J. Phys. Chem. B., (2004), 108, 1255-1266.
[6] Simulations were carried out using MS Modeling 3.2 from Accelrys Inc. of San Diego.
[7] M. P. Allen and D. J. Tildesley, Computer simulation of liquids, Oxford university press, 2003, 183-184.
[8] N. S. Martys, Journal of Rheology, 2005, Vol. 49, No. 2, 401-424.
[9] R. D. Groot and K. L. Rabone, Biophysical Journal, 2001, Vol. 81, 725-736.
[10] J. W. Goodwin and R. W. Hughes, Rheology for Chemists an Introduction, RSC press, 2000, 216.
[11] A. A. Zaman, M. Bjelopavlic and B. M. Moudgil, J. Colloid and Interface Science, 226, 290-298 (2000)